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(54) Process for the rapid determination of the resistance of corrosion of an electrophoretic coating, and apparatus for its accomplishment .

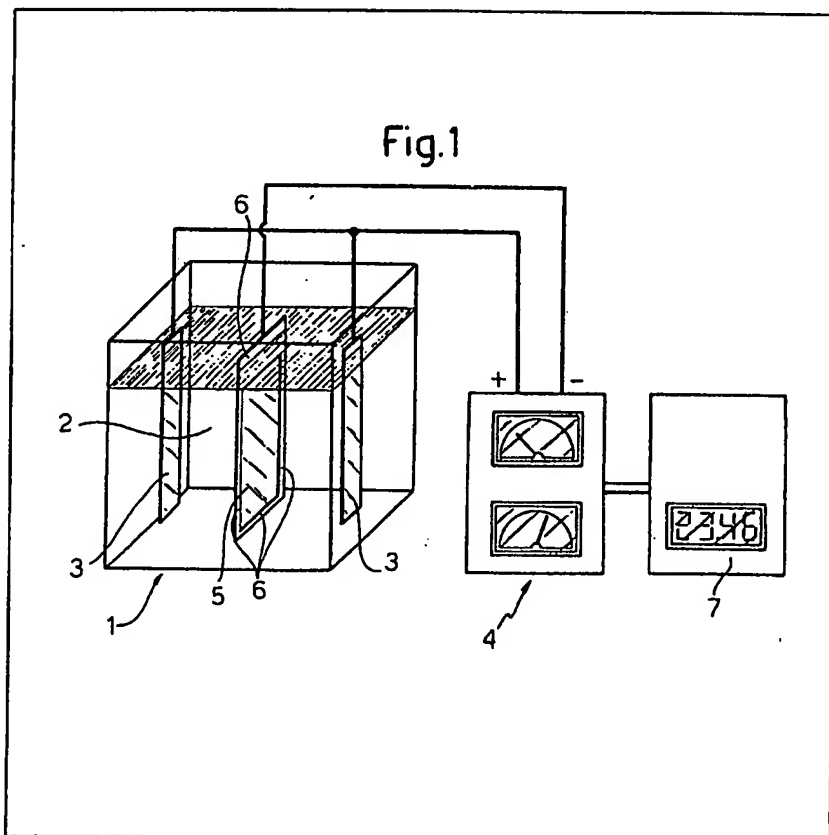
(57) A process for a rapid determination of the resistance to corrosion of an electrophoretic coating, which process comprises at least a stage comprising the following operations:—

Immersing a specimen comprising a metal support 6 coated with the coating 5 into an electrolyte 2 of an electrolytic cell, into which a solution

of a hydroxide has been introduced to obtain an alkaline medium in the cell with a pre-determined hydroxide concentration,

electrically connecting the specimen to the negative pole of the current feeder electrode of the said cell, so that the specimen itself forms the cathode of the cell, and

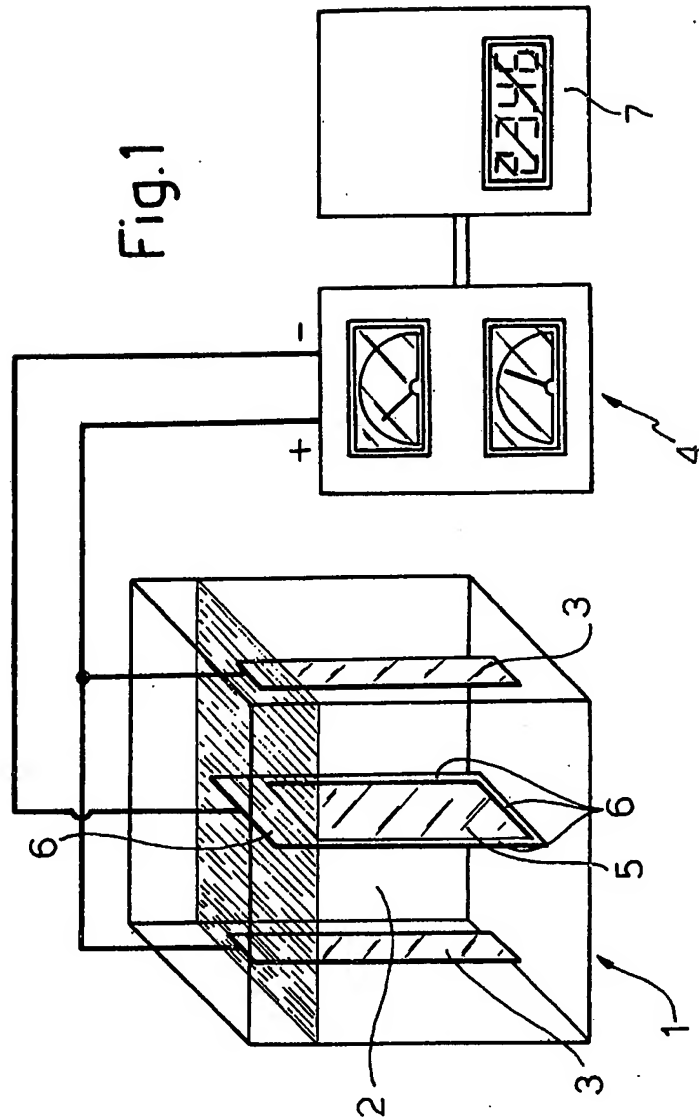
determining the time required to detach a portion of the coating from the support, and to cause the corrosion of the support until a predetermined current is obtained between the electrodes of the cell.



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Fig.1



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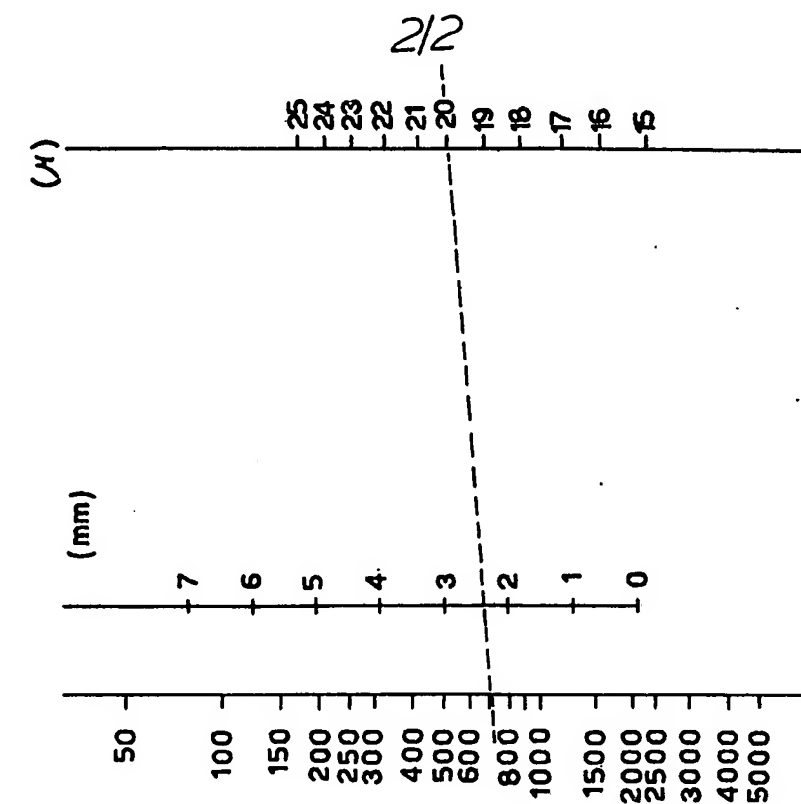


Fig.3

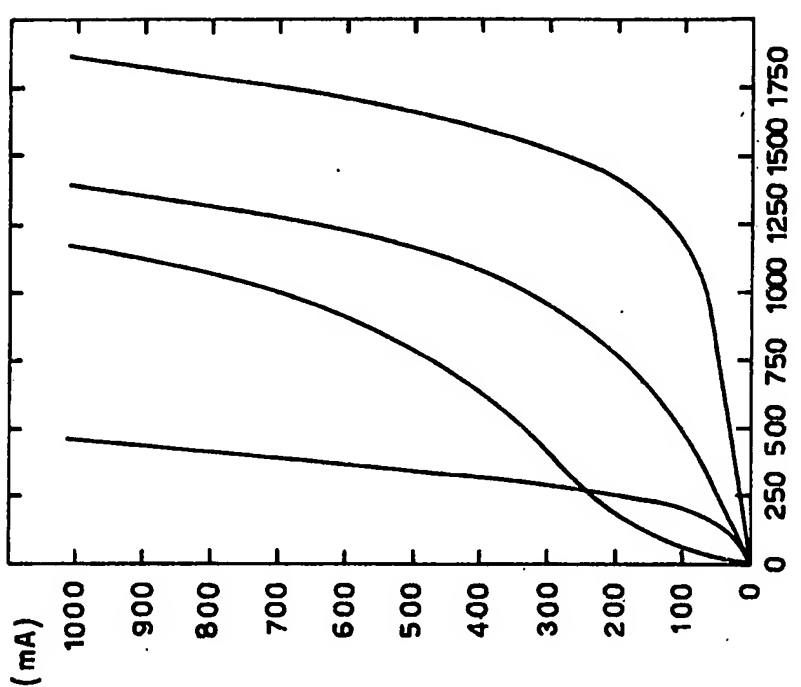


Fig.2

SPECIFICATION

Process for the rapid determination of the resistance to corrosion of an electrophoretic coating, and apparatus for its accomplishment.

5 The present invention relates to a process for the determination of the resistance to corrosion of an electrophoretic coating, obtained both by anodic and cathodic treatments, by means of which it is possible to carry out on specimens very
10 rapid measurements of the resistance to corrosion, such as those which are required for the control of industrial painting lines.

As it is well-known, processes of deposition of resin layers of various types on metal supports by means of anodic and cathodic electrophoresis are
15 widely used in painting, in particular in the painting of motor vehicle bodies; the first layer, which is in direct contact with the surface of the body, is, in fact, constituted by a resin deposited by electrophoresis, and to this end usually the
20 anodic electrophoresis is utilized, with which it is possible, for example, to obtain a first coating of polybutadiene resins having thicknesses up to $30 \div 35$ micron.

25 In controlling such painting processes it is quite important to evaluate the quality of the electrophoretic coating, in order to ensure a perfect protection against corrosion agents of the support onto which the coating has been deposited.

As it is well-known, the determination of the resistance to corrosion of the said coatings is usually carried out by exposing, first, specimens formed by a suitably coated plate of the material
35 of the support, to the action of a corrosion agent (formed, usually, by a saline fog obtained from a solution of sodium chloride in water), and then measuring the dimensions of the traces of corrosion thus obtained, according to the modalities fixed by the norm ASTM B 117.

Therefore, the corrosion takes place electrochemically (oxidation of the iron and reduction of the oxygen), by the action of the moisture and the oxygen which contact the
45 surface of the specimen through the pores of the coating or through suitable notches formed in this latter); the speed with which this phenomenon takes place is considerably increased by the presence of the sodium chloride in the said fog.

50 The evaluation of the resistance to corrosion by means of this process gives rise to numerous disadvantages.

First of all, the time required for the accomplishment of the process is quite long, in
55 the order of hundreds of hours; this is, in fact, the time which is necessary, in the test conditions described, for obtaining traces of corrosion having measurable dimensions.

Moreover, this process cannot be used for
60 obtaining, in a continuous manner, data useful for the control of a continuous painting line in which it is necessary to undertake an action as soon as a disadvantageous variation of the quality of the deposited coatings takes place; in fact, because of

65 the considerably long time required for carrying out each test, actions can be undertaken only after having painted a considerable quantity of products whose coating is of unacceptable quality.

Finally, the process described hereinabove
70 usually does not allow a very accurate quantitative evaluation of the resistance to corrosion, because of the rather high dispersion of the results to which the process gives rise; therefore, with this process it is not possible to obtain data suitable for a rigorous comparison of coatings whose characteristics are little different.

It is an object of the present invention to provide a process for quickly determining the resistance to corrosion of an electrophoretic
80 coating, which will allow avoiding the disadvantages mentioned hereinabove.

Another object of the present invention is to provide an apparatus for the accomplishment of the process according to the invention.

85 The process according to the present invention is characterized in that it comprises at least a stage including the following operations: immersing a specimen comprising a metal support coated with the said coating into an electrolyte of an electrolytic cell, into which a hydroxide has been introduced in solution to obtain in the said cell an alkaline medium with a pre-established concentration of hydroxide, electrically connecting the said specimen to the positive pole of the
95 current feeder of the said cell, so that the specimen itself will form the cathode of the cell, and maintaining the said specimen within the said electrolyte for the time which is necessary to produce the detachment of a portion of the said
100 coating from the support and to let the corrosion of the support go on till an electric conductivity between the electrodes of the said cell is obtained which is apt to establish between them a circulation of a pre-established current.

105 For a better understanding of the process according to the present invention, the fundamental stages of the process will now be described in detail with reference to an embodiment of an apparatus suitable for the accomplishment of the process, shown by way of non limiting example in the accompanying drawings, in which:

FIGURE 1 is a diagrammatic perspective view of the apparatus according to the invention,

115 FIGURE 2 shows some curves of experimental results obtained by means of the apparatus shown in Fig. 1, and

FIGURE 3 shows a nomogram apt to allow an immediate comparison of the data obtained by means of the process according to the invention with those obtained by means of a prior art process.

Before describing the stages of the process according to the invention it is suitable to examine the apparatus for the accomplishment of the said
125 process.

This apparatus substantially comprises an electrolytic cell, indicated generally by reference numeral 1, filled with an electrolyte 2 obtained

substantially by means of a solution of a hydroxide in water; in order to provide an alkaline medium in the said cell.

5 The said hydroxide may be of any metal, for example a sodium hydroxide; although it is preferable to reach in the electrolyte a concentration of hydroxide of about 1,25 equivalent grams/liter of OH, the said concentration is not critical. It has been noticed
10 that when the hydroxide is sodium hydroxide the concentration of this hydroxide should conveniently be of about 50 g/l.

The cell is provided with two anodes 3 of any suitable material, for example, steel, disposed
15 adjacent two opposite walls of the cell and electrically connected to the positive pole of a suitable current feeder 4. The said cell is provided also with means (not shown) apt to support within the electrolyte a specimen 5 and to connect it
20 electrically with the negative pole of the feeder 4, in order that it forms the cathode of the cell; conveniently, the specimen 5 is arranged between the anodes 3, as can be clearly seen in Fig. 1.

The said specimen is formed by lamination of
25 the support material on which the coating being tested has been deposited by electrophoresis; the coating may be any layer deposited by electrophoresis, either anodic or cathodic; thus, the layer may be a thin layer of any resin apt to be
30 deposited by such treatment. In the case of anodic electrophoresis, the said coating may conveniently be formed by a layer of polybutadiene resins, having the maximum thickness of 30—35 micron.

Conveniently, the specimen 5 has its edges 6
35 covered by a suitable protection material, such as paraffine, in order both to exclude the edge regions from the test and to define on it two opposite substantially rectangular surfaces having a pre-established area; an electric conductor may
40 be connected, in any suitable way, to the said support and serves for an immediate electric connection of the specimen to the said means. These latter may have any structure, provided they are apt to support the specimen in a pre-
45 established position within the cell 1 and to connect it electrically to the feeder 4; they may comprise guides, stops, electric connection members and the like, normally used in means of this type.

50 The apparatus may also comprise a time counter 7, apt to be activated when the specimen 5 is introduced into the cell 1 (or when current is supplied by the feeder 4) and to be deactivated by an electric signal emitted when a pre-
55 established current flows between the electrodes 3 and 5 of the cell. The said counter is conveniently an electronic counter, for example of the digital type, activable manually. In order to generate the said deactivation electric signal, cell
60 1 and electrodes 3 and 5 are part of an electric circuit (not shown) comprising two points whose voltage difference is compared with a reference voltage; the said deactivation signal is emitted when the said reference voltage is reached
65 between the said two points. The circuit is

conceived in such a way that the said condition (equality between the voltage differences between the said two points and the reference voltage) will arise only when between the electrodes 3 and 5 a
70 current circulates which has a pre-established value, for example 1 ampere.

The process according to the invention, accomplished by means of the apparatus described hereinabove, takes place in the
75 following manner.

A specimen 5, prepared as described hereinabove, is introduced into the cell 1 and is connected to the said support means, and at the same time the time counter 7 is activated.

80 The solution of the electrolyte 2 passes through the pores of the coating (or through the eventual notches formed in the coating in accordance with modalities fixed by some standardized norms) and the corrosion of the support initiates. The
85 corrosion takes place according to the same cathodic etching mechanism according to which it proceeds both in the conditions of the outer ambient and in the the saline fog process described before.

90 However, the corrosion takes place at a very high speed, owing both to the alkaline medium created by the addition of the hydroxide to the electrolyte and the cathodic connection of the specimen. In fact, it has been found that when in
95 the interface coating/support surface there is, from the chemical point of view, a high basicity and; from the electrical point of view, a distribution of negative voltages (cathodic areas), the detachment of the coating occurs easily and the corrosion rate as particularly high.

100 It has, however, to be noted that, on the other hand, the said two conditions are not created artfully without any connection with the mechanism of the corrosion in the case of the exposition of the specimen to the outer ambient or to that of the saline fog. In fact, it has been found that in both said cases the corrosion can proceed, even at a very modest rate, only when cathodic
105 areas are created, through normal electrochemical phenomena, in the interface coating/support surface; it has been noticed that in these areas the basicity is always rather high and higher than that of the other areas.

Therefore, with the process of the present
115 invention modalities have been contrived for increment, to a substantial extent, the rate at which normally the corrosion of the coating proceeds in the outer ambient, without substantially altering the mechanism with which
120 the corrosion takes place in the said ambient. It follows that the results obtainable by means of the process according to the invention, not only give a quantitative indication of the resistance to corrosion as if it was taking place in the outer ambient, but also give indications comparable with those which are obtained by means of the saline fog exposition process described
125 hereinabove.

As the corrosion of the specimen proceeds and
130 consequently the area of its surfaces loosing their

coating increases, there is an increase of the current which flows in the electrolyte 2 between the electrodes 3 and 5.

On the ground of the process according to the invention, the resistance to corrosion of the specimen is evaluated on the basis of the time required to let the corrosion proceed to a sufficient degree for obtaining a flow of a pre-established current in the electrolyte and between the electrodes. The value of this current may be chosen in any way whatever, for example by means comparison with the saline fog test process. With an electrolytic cell having the capacity of about two litres and with specimens coated with a polybutadiene resin and having surfaces of 150 x 70 mm (free surfaces between the edges 6 of about 134 cm²), with steel anodes having the dimensions 25 x 120 x 0,8 mm and disposed at a distance of 120 mm, and with a concentration of sodium hydroxide of 50 g/l in the electrolyte, it has been deemed suitable to fix at 1 ampere the value of the said current.

Under these circumstances, the time required for evaluating the resistance to corrosion of each specimen was in the order of 30 minutes: the results obtained in the said experimental conditions are shown in the diagrams of Fig. 2, whose curves indicate the values of the currents measured between the electrodes 3 and 5, as a function of the test time, for four different specimens. From these results it can be noticed that for current values of 1 ampere there is a considerable differentiation between the resistances to corrosion of the various specimens; obviously, to the increase of the test time required for causing a 1 ampere current to flow between the electrodes, correspond higher resistances to corrosion.

With the process according to the present invention, when the aforementioned condition (flow of a pre-established current between the electrodes 3 and 5) is obtained, between the said points of the electric circuit described hereinabove there is also obtained a voltage difference sufficient for the time counter to emit a desactivation signal. In this way, the count of the time is stopped and the operator can, at any moment, carry out on the counter the reading of the test time which, as said before, constitutes a parameter proportional to the resistance to corrosion.

Obviously, it is possible to put into relation the results obtained by means of the process according to the invention with those obtained by means of the conventional process with exposition to a saline fog, in order to ascertain to which dimensional value of the corrosion trace on a specimen subjected to tests with this latter process corresponds, in the same experimental conditions, the test time evaluated, as indicated above, with the first mentioned process. This correlation can be found in various manners by means of experimental comparison tests which do not require any further description.

By way of example, in the nomogram of Figure

4 there are indicated the results of the correlation found between the two processes by means of tests carried out in the aforementioned experimental conditions on specimens coated with polybutadiene resin coatings having thicknesses between 15 and 25 micron; the results shown in Figure 4 relate to the comparison by means of tests carried out in accordance with the saline fog exposition process in which the duration of the exposition was of 200 hours.

The comparison of the results obtained with the two processes may be carried out by means of a straight line like the one traced by a dashed line in the nomogram; as indicated by this straight line, to a test carried out in accordance with the process of the invention, whose time is indicated by a point of the scale on the left-hand side and whose coating thickness is indicated by a point of the scale on the right-hand side, corresponds a test carried out by means of the saline fog exposition process which leads to a dimension of the corrosion trace which can be read on central scale, at the point at which it is intersected by the straight line joining the aforementioned points.

It is clear that each of the described stages of the process according to the present invention may be modified and the succession of these stages may be varied, without departing from the scope of the invention.

95 CLAIMS

1. A process for a rapid determination of the resistance to corrosion of an electrophoretic coating, which process comprises at least a stage comprising the following operations: immersing a specimen comprising a metal support coated with the coating into an electrolyte of an electrolytic cell, into which a solution of a hydroxide has been introduced to obtain an alkaline medium in the cell with a pre-determined hydroxide concentration, electrically connecting the specimen to the positive pole of the current feeder electrode of the said cell, so that the specimen itself forms the cathode of the cell, and maintaining the specimen within the said electrolyte for the time required to detach a portion of the coating from the support and to cause the corrosion of the support until an electric conductivity between the electrodes of the cell is obtained which establishes between them a pre-determined current.

2. A process as claimed in claim 1 wherein the electrolyte has a hydroxide in a concentration of between 0.2 and 3 equivalent g/l.

3. A process as claimed in claim 1 or claim 2 wherein the hydroxide is sodium hydroxide and the concentration of sodium hydroxide in the electrolyte is between 8 and 120 g/l.

4. A process as claimed in any one of the preceding claims wherein the said time is the time which is necessary to produce the detachment of a portion of the coating from the support and sufficient to obtain between the electrodes of the cell an electric conductivity which causes a current of 1 ampere to flow between the electrodes.

5. An apparatus for the rapid determination of the resistance to corrosion of an electrophoretic coating, which apparatus comprises an electrolytic cell into the electrolyte of which a solution of a hydroxide has been introduced to obtain an alkaline medium in the cell with a pre-determined hydroxide concentration, the cell being arranged to use as its cathode a specimen comprising a metal support coated with the coating, and a measuring means to measure the current flowing between the electrodes of the cell, the resistance to corrosion of the specimen being measured on the basis of the time required to produce the detachment of a portion of the coating to an extent sufficient to obtain between the electrodes of the cell an electric conductivity which causes a pre-determined current to flow between them.
6. An apparatus as claimed in claim 5 which comprises a time counter which activates when the specimen is introduced into the cell and which is deactivated by an electric signal which is emitted when the pre-determined current flows between the electrodes of the cell.
7. An apparatus as claimed in claim 6 wherein the electric signal is emitted when a pre-determined reference voltage is obtained between the electrodes and the electrolyte of the electrolytic cell.
8. A process as claimed in claim 1 substantially as hereinbefore described with reference to the accompanying drawings.
9. An apparatus as claimed in claim 4 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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